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ELECTRICAL CONDUCTIVITY IN THE FUSED SALT SYSTEM $PbCl_2$-NaCl-KCl

S.A. Mikhail, C.R.K. MacLean and A.H. Webster
Physical Chemistry Section
Extractive Metallurgy Laboratory

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ELECTRICAL CONDUCTIVITY IN THE FUSED SALT SYSTEM $PbCl_2$-NaCl-KCl

by

S.A. Mikhail*, C.R.K. MacLean** and A.H. Webster*

ABSTRACT

Electrical conductivity measurements in the molten salt system $PbCl_2$-NaCl-KCl was measured using a silica glass capillary conductivity cell with Pt electrodes and an ac conductivity bridge. The specific conductivity increased linearly with temperature. Within the range of compositions examined, specific conductivity decreased with increasing KCl content and increased with increasing $PbCl_2$ content. Isoconductivity lines within the ternary liquid region were determined for seven temperatures in the range 400-550°C. A 12-term polynomial equation correlating conductivity with temperature and composition was fitted to the experimental values for specific conductivity. Molar and equivalent conductivities were determined for 500°C. The equivalent conductivities could be interpreted in terms of the formation of lead-chloride complex ions for compositions near the $PbCl_2$-KCl boundary.

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*Research Scientists and **Technologist, Physical Chemistry Section, Extractive Metallurgy Laboratory, Mineral Sciences Laboratories, CANMET, Energy, Mines and Resources Canada, Ottawa.

CONDUCTIVITÉ DANS LE SYSTÈME CONSTITUÉ DE $PbCl_2$-NaCl-KCl EN FUSION

par

S.A. Mikhail*, C.R.K. MacLean** et A.H. Webster*

RÉSUMÉ

On a mesuré la conductivité d'un système consituté de $PbCl_2$-NaCl-KCl en fusion, à l'aide d'une cellule capillaire en verre de silice munie d'électrodes en Pt et d'un pont conductimétrique à courant alternatif. La conductivité spécifique augmentait de façon linéaire avec la température. Dans les plages de composition examinées, la conductivité spécifique diminuait de façon inversement proportionnelle avec la teneur en KCl et augmentait de façon proportionnelle avec la teneur en $PbCl_2$. On a déterminé les lignes de même conductivité dans la région liquide ternaire, à sept températures dans la plage comprise entre 400 et 550°C. On a mis au point une équation polynôme à 12 termes mettant en corrélation la conductivité avec la température et la composition, permettant de décrire les valeurs expérimentales de la conductivité spécifique. On a déterminé les conductivités molaire et équivalente à 500°C. On peut expliquer les conductivités équivalentes par la formation d'ions complexes plomb-chlorure pour des compositions au voisinage de la limite $PbCl_2$-KCl.

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*Chercheur et **Technologiste, Section de la chimie physique, Laboratoire de métallurgie extractive, Laboratoires des sciences minérales, CANMET, Ministère de l'Energie, des Mines et des Ressources, Ottawa, Canada.

INTRODUCTION

Recent trends in environmental protection and more stringent plant hygiene requirements have revived interest in various metallurgical processes which were considered less economical and hence less attractive for research and development. The production of metallic lead by molten salt electrolysis is one of several processes that have attracted some attention in the last few years. In this process, molten lead chloride is electrolysed in an electrolytic cell where the metallic lead collects at the cathode and chlorine gas evolves at the anode. Molten lead chloride on its own, however, does not possess the optimum characteristics of a successful electrolyte. Above its relatively high melting point (498°C), lead chloride has a fairly high vapour pressure and dissolves a small amount of metallic lead. These undesirable characteristics can be improved by the addition of alkali chlorides such as LiCl, KCl and NaCl.

Extensive work at the U.S. Bureau of Mines (1-3), both on bench and mini-pilot plant scales, demonstrated that the molten alkali chloride solutions LiCl-KCl and NaCl-KCl may be used as solvents for $PbCl_2$ in the electrolysis process. The study recommended the use of the LiCl-KCl eutectic composition at 450°C on the basis of the high solubility of $PbCl_2$ in this melt and the high electrical conductivity of the electrolyte at this temperature. In the first part of the present work (4), the electrical conductivity in the ternary system $PbCl_2$-LiCl-KCl was studied for the first time. The isoconductivity lines within the ternary liquid region were determined and ternary sections at 350, 375, 400, 425, 450, 475, 500 and 525°C were plotted. The specific conductivity was found to increase steadily with temperature and with LiCl content in the mixture. Molar and equivalent conductivities were also computed using density data reported by Gutiérrez and Toguri (5).

A major disadvantage of using LiCl-KCl as a solvent is the highly hygroscopic nature of LiCl which can lead to substantial hydrolysis at high temperatures. In the conductivity studies, besides several precautions in handling the starting materials, it was found essential to subject the mixtures to an extensive HCl-Ar-vacuum-filtration treatment at high temperature, following Laitinen's procedure (6), to remove any traces of moisture. In the present work, LiCl was replaced by NaCl and the conductivity measurements in the system $PbCl_2$-NaCl-KCl were made in the

temperature range 388-603°C within the ternary liquid region.

Electrical conductivities have been determined previously for the three binary systems of the $PbCl_2$-NaCl-KCl system. Lantratov and Nikiseeva (7) and Bloom and Heymann (8) found minima in the specific conductivities of the $PbCl_2$-KCl system at about 30 mol % $PbCl_2$. Van Artsdalen and Yaffe (9) showed that the specific conductivity in the system KCl-NaCl increased monotonically from KCl to NaCl. Electrical conductivities in the system $PbCl_2$-NaCl have been reported by Bloom and Macky (10). Critical summaries of the properties of the systems $PbCl_2$-KCl (11), $PbCl_2$-NaCl (11) and KCl-NaCl (12) have been given by Janz and co-workers.

The phase diagram of the system $PbCl_2$-NaCl-KCl was determined experimentally by Treis (13) and was recently calculated from the binary components by Skeaff et al. (14) who also calculated the activities and vapour pressures at different temperatures. Densities were measured by Gutiérrez and Toguri (5) in the temperature range 487-857°C. Some thermodynamic properties were determined by Hagemark et al. (15) on the basis of emf measurements.

MATERIALS AND EXPERIMENTAL PROCEDURE

The starting materials used in the present work were "Baker Analysed" reagent grade NaCl and KCl crystals and $PbCl_2$ (99.9%) powder. Semi-quantitative spectrochemical analysis indicated the following major impurities in the NaCl: Fe(0.009%), Cu(0.004%) and Ca(0.002%), in the KCl: Fe(0.001%), Ca(0.001%) and Cu(0.005%) and in the $PbCl_2$: Al(0.01%), Fe(0.001%), Si(0.001%), Cu(0.007%), Ag(0.0009%) and Mg(0.0003%). All materials were dried in vacuum at 150°C for several hours and stored in a dry box. Weighing, mixing and handling of the starting mixtures were done inside the dry box.

The equipment and procedure used in the conductivity measurements were given in detail in a previous report (4). The measurements were conducted using the two frequencies provided by the conductivity bridge, namely 1 and 3 kHz and the difference was around 0.1%. The cell constants for the capillary cells were in the order of 550-750 cm^{-1}. The cell constant was measured before and after each series of experiments and the difference was less than 0.4%.

RESULTS AND DISCUSSION

The electrical conductivities were measured for several ternary compositions in the temperature range 388-603°C. The specific conductivity, κ, was determined by substituting the electrical conductance, k (siemens), and the cell constant, K_{cell} (cm^{-1}), in the following equation:

$$\kappa = k.K_{cell} \qquad (1)$$

The cell constant was determined from conductance measurements on aqueous KCl solutions for which specific conductivity data is available (16).

In the ternary $PbCl_2$-NaCl-KCl, two compositional parameters, y and t, were used to identify each composition:

$$y = 1 - X_{PbCl_2} = X_{NaCl} + X_{KCl}$$

and

$$t = \frac{X_{NaCl}}{X_{NaCl} + X_{KCl}}$$

where X is the mole fraction. Therefore, in the ternary system, a y value of 1 represents the boundary system NaCl-KCl, a t value of 0 represents the system $PbCl_2$-KCl, and a t value of 1 represents the system $PbCl_2$-NaCl.

In preliminary experiments, the conductivity of the composition 48.77 mol % KCl - 51.23 mol % NaCl was measured at different temperatures between 660 and 800°C and the results were compared with those obtained by Van Artsdalen and Yaffe (9). A maximum difference of 0.8% was found at the higher temperatures.

Twenty-three mixtures, within the composition range t = 0.2 to 0.7 and $PbCl_2$ mole fraction of 0.3 to 0.7, were examined in the ternary system. In Table 1, the summary of the results is presented as the least squares fit of the conductivity versus temperature according to the following equation:

$$\kappa = a + bT \qquad (2)$$

Table 1. Least squares fit of the electrical conductivity (κ, $S.cm^{-1}$) vs temperature (T,K) for various values of the composition parameters t and y for the system $PbCl_2$-NaCl-KCl

$PbCl_2$ Mole fraction (1-y)	Temp. Range, °C	$\kappa = a + bT$		Standard Error of Estimate	Correlation Coefficient
		-a	$bx10^3$		
t=0.20					
0.40	449-550	1.6980	3.621	±0.0017	0.9999
0.50	403-548	1.7348	3.746	0.0032	0.9999
0.60	432-549	1.7631	3.869	0.0022	0.9999
0.70	430-549	1.9661	4.219	0.0041	0.9997
t=0.30					
0.40	449-548	1.7819	3.799	0.0030	0.9998
0.50	388-547	1.8254	3.915	0.0061	0.9996
0.60	416-547	1.8619	4.038	0.0059	0.9995
0.70	414-547	1.9689	4.257	0.0046	0.9997
t=0.40					
0.40	476-549	1.7623	3.844	0.0032	0.9995
0.50	425-548	1.7522	3.889	0.0046	0.9997
0.60	401-549	1.9024	4.152	0.0076	0.9994
0.70	409-548	2.0708	4.426	0.0076	0.9994
t=0.50					
0.30	550-603	2.0986	4.291	0.0080	0.9963
0.40	511-568	1.6334	3.771	0.0026	0.9996
0.50	458-555	1.7604	3.959	0.0037	0.9996
0.60	400-549	1.9646	4.276	0.0071	0.9995
0.70	407-548	2.1112	4.513	0.0053	0.9997
t=0.60					
0.50	492-549	1.6742	3.908	0.0021	0.9997
0.60	413-548	1.9502	4.299	0.0057	0.9996
0.70	413-548	2.0736	4.489	0.0052	0.9997
t=0.70					
0.50	499-550	1.7065	4.034	0.0013	0.9999
0.60	426-550	1.9330	4.340	0.0047	0.9997
0.70	421-548	2.0972	4.565	0.0044	0.9998

where κ is the specific conductivity in siemens.cm^{-1} (ohm^{-1}cm^{-1}), T is the temperature in Kelvin and a and b are constants. The temperature range in which the conductivity of each composition was measured was limited by the ternary liquidus temperature and by $PbCl_2$ volatilization (14). Throughout the experiments, it was noticed that fuming started when the temperature exceeded 500°C and the $PbCl_2$ mole fraction exceeded 0.5. The total experimental uncertainty in the cell constant, temperature and salt composition was estimated to be less than ±2%.

Typical results of two series of experiments for the conductivities of compositions with low (t=0.2) and high (t=0.6) NaCl contents and different mole fractions of $PbCl_2$ are presented in Figure 1. It is apparent that the conductivity in this system is mainly dependent on temperature and to a lesser extent on composition. In comparison to LiCl (4), the influence of NaCl on the conductivity was less pronounced. For instance, for a solution containing 50 mol % $PbCl_2$ at 500°C, a change in t from 0.3 to 0.7 resulted in an increase in the conductivity of 34% in the system $PbCl_2$-LiCl-KCl but only 15% in the system $PbCl_2$-NaCl-KCl. For lower $PbCl_2$ contents the difference would be even higher. This reflects the lower conductivity of NaCl, which is closer to the conductivities of $PbCl_2$ and KCl than is the relatively high conductivity of LiCl.

The decrease in conductivity with increasing KCl content (lower t) is quite evident in Figure 1. The influence of $PbCl_2$ on the conductivity is relatively larger at the KCl-rich side of the system, as shown in Figure 1, where the increase in conductivity with increasing $PbCl_2$ content is greater at t = 0.2 than at t = 0.6. Specific conductivity in the binary system $PbCl_2$-KCl (7,8) has a minimum at about 0.3 mole fraction $PbCl_2$ and increases as the lead chloride composition is approached. The increase in conductivity with increasing $PbCl_2$ content in melts containing high ratios of KCl/NaCl is therefore consistent with the behaviour of the $PbCl_2$-KCl boundary system.

The conductivity of each of the compositions investigated was calculated at seven selected temperatures, namely 400, 425, 450, 475, 500, 525 and 550°C by substituting the relevant constants a and b from Table 1. At each of the selected temperatures, the relationship between κ and t was plotted for each X_{PbCl_2} and the relationship between κ and X_{PbCl_2} was plotted for each t. The isoconductivity compositions were then determined graphically. Figures 2 to 8 show the isoconductivity lines within the

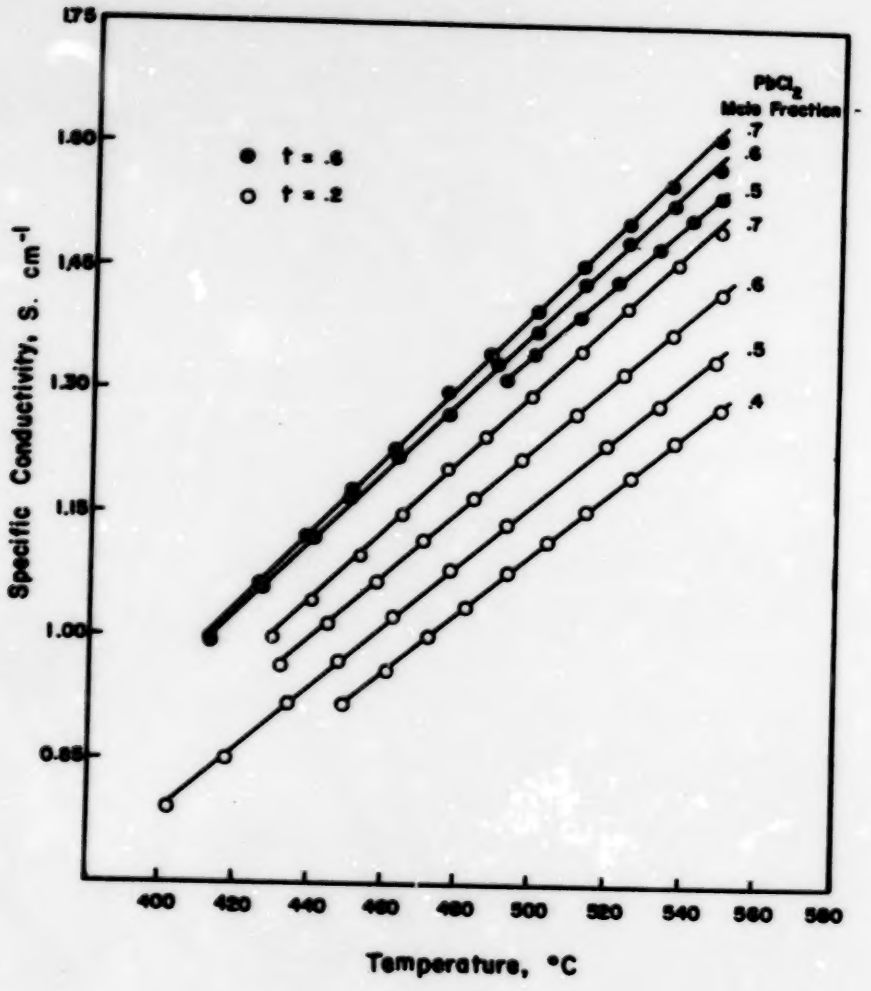

Fig. 1 - Temperature dependence of the conductivity in the system $PbCl_2$-NaCl-KCl

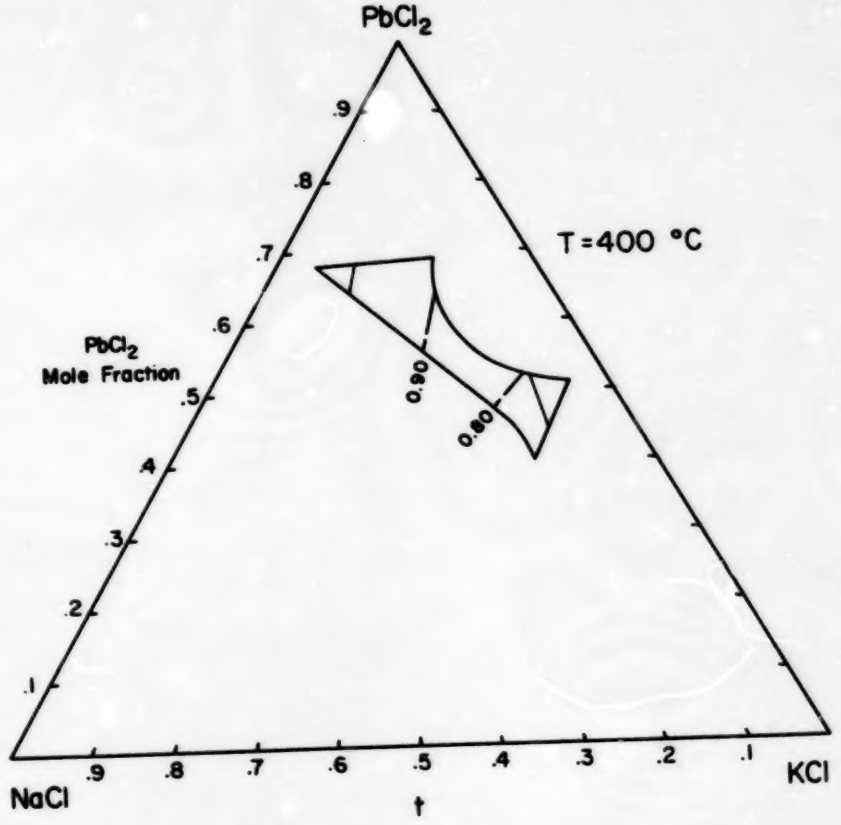

Fig. 2 - Isoconductivity lines in the system $PbCl_2$-NaCl-KCl at 400°C.

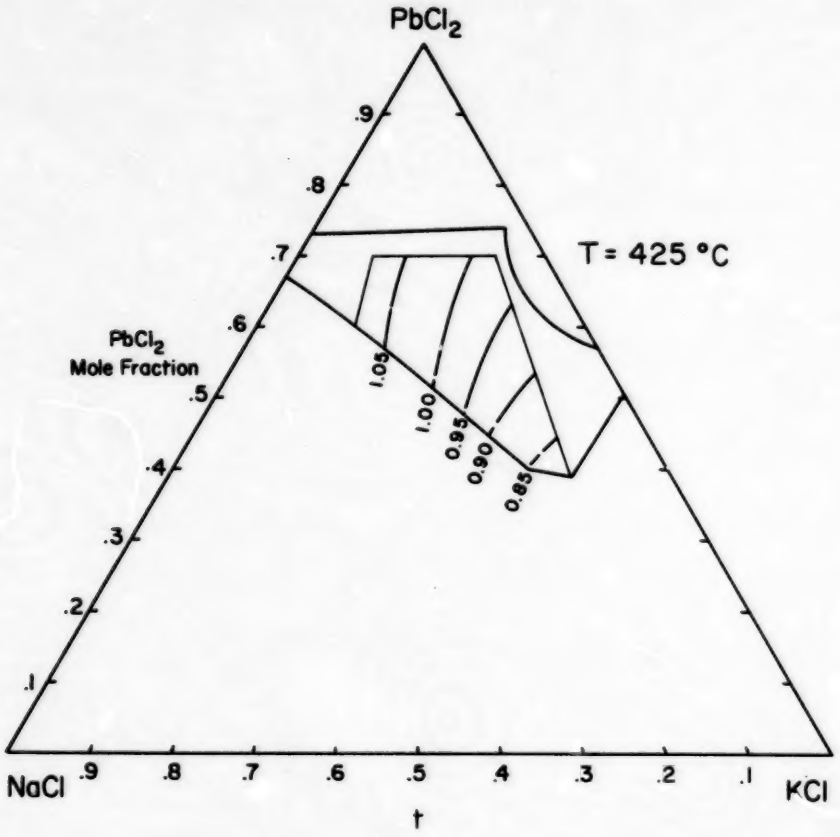

Fig. 3 - Isoconductivity lines in the system $PbCl_2$-NaCl-KCl at 425°C.

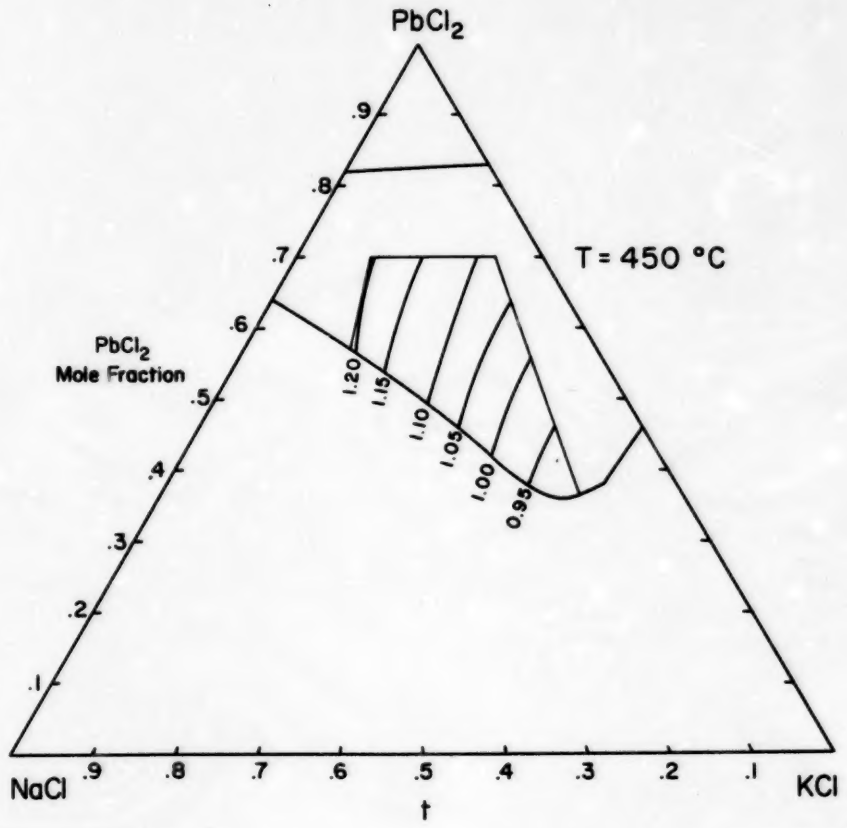

Fig. 4 - Isoconductivity lines in the system $PbCl_2$-NaCl-KCl at 450°C.

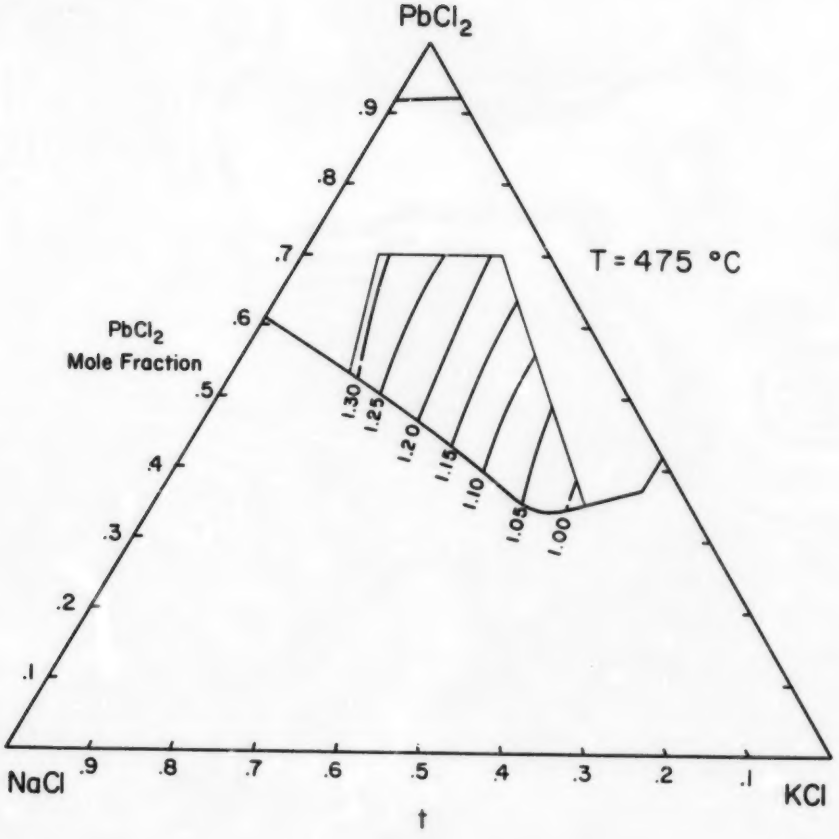

Fig. 5 - Isoconductivity lines in the system $PbCl_2$-NaCl-KCl at 475°C.

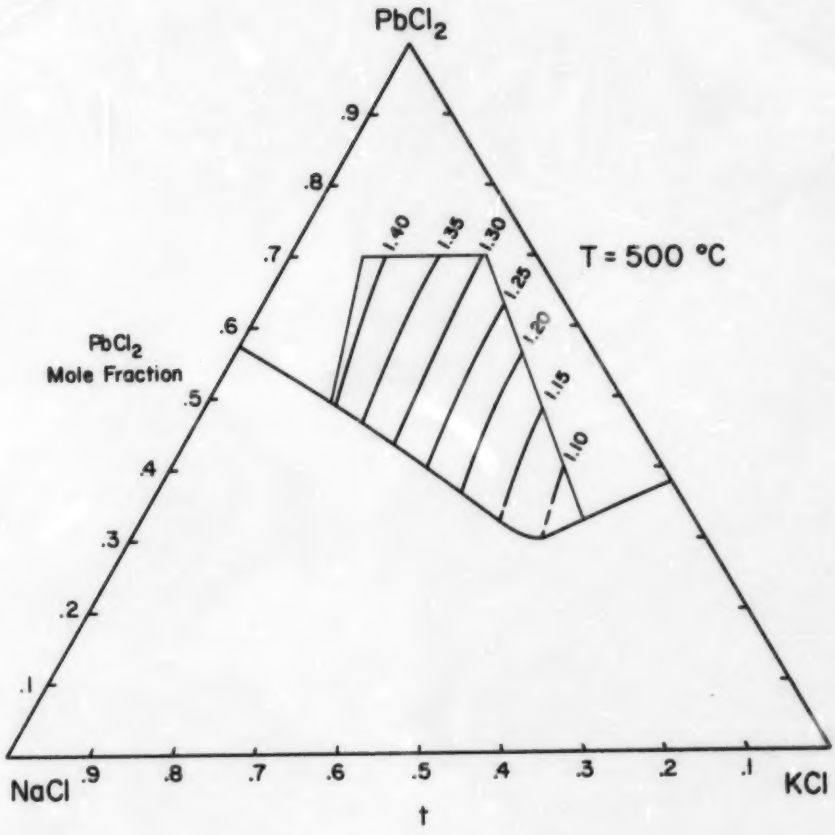

Fig. 6 - Isoconductivity lines in the system $PbCl_2$-NaCl-KCl at 500°C.

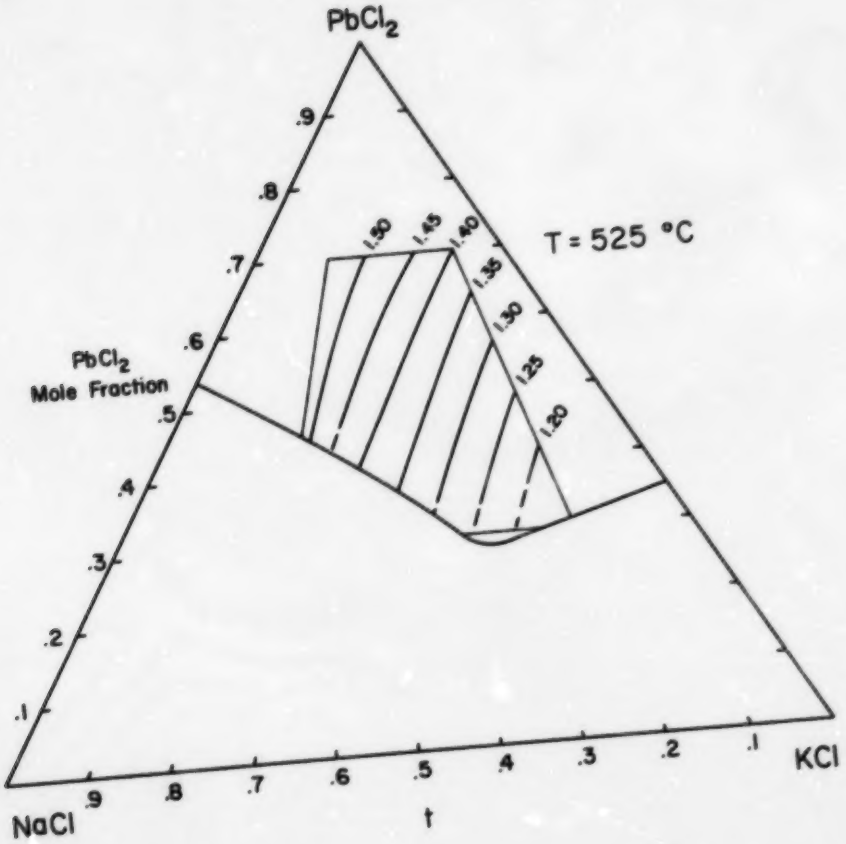

Fig. 7 - Isoconductivity lines in the system $PbCl_2$-NaCl-KCl at 5

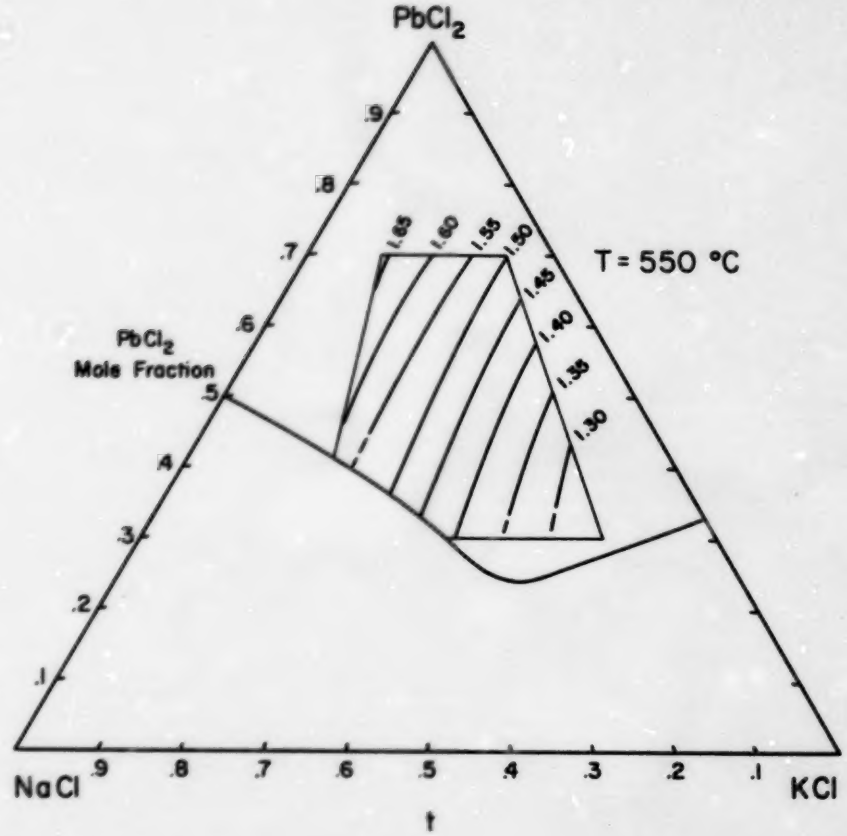

Fig. 8 - Isoconductivity lines in the system $PbCl_2$-NaCl-KCl at 550°C.

ternary liquid regions at the different temperatures. The direction of these lines indicated that, besides the temperature, the KCl content has the most noticeable influence on the conductivity in this ternary system.

The experimental values obtained for the specific conductivities ($S.cm^{-1}$) of the different compositions at different temperatures (231 data points) were found to fit the following equation:

$$\kappa = [a_0 + a_1y + a_2y^2 + a_3yt + a_4yt^2 + a_5ty^2] + T[b_0 + b_1y + b_2y^2 + b_3yt + b_4yt^2 + b_5ty^2] \quad (3)$$

where $a_0 = -2.975987$ $\quad b_0 = 0.58105967 \times 10^{-2}$

$a_1 = 5.5736671$ $\quad b_1 = -0.83713087 \times 10^{-2}$

$a_2 = -5.6118478$ $\quad b_2 = 0.73301975 \times 10^{-2}$

$a_3 = -4.2370282$ $\quad b_3 = 0.62749975 \times 10^{-2}$

$a_4 = 1.9517599$ $\quad b_4 = -0.22277599 \times 10^{-2}$

$a_5 = 4.7409480$ $\quad b_5 = -0.57326596 \times 10^{-2}$

Standard error of estimate = $\pm 0.0065\ S.cm^{-1}$

Only two experimental points deviated from the values predicted by Equation 3 by more than 1.5% (<2.3%) and therefore the equation may be used to determine (within the error range) the specific conductivity of any ternary solution at any temperature within the investigated region. A comparison between the experimental and the predicted values is afforded by Figure 9.

The molar conductivity, Λ_M, was calculated using the expression,

$$\Lambda_M = \kappa.V_M, \quad (4)$$

where κ is the specific conductivity and V_M is the molar volume. The molar volume was determined from density data reported by Gutiérrez and Toguri (5) for compositions within the ternary system, by Boardman et al. (17) for the $PbCl_2$-KCl binary, and by Bloom et al. (18) for the $PbCl_2$-NaCl binary, using the expression,

$$V_M = \frac{\sum X_i M_i}{\rho}, \quad (5)$$

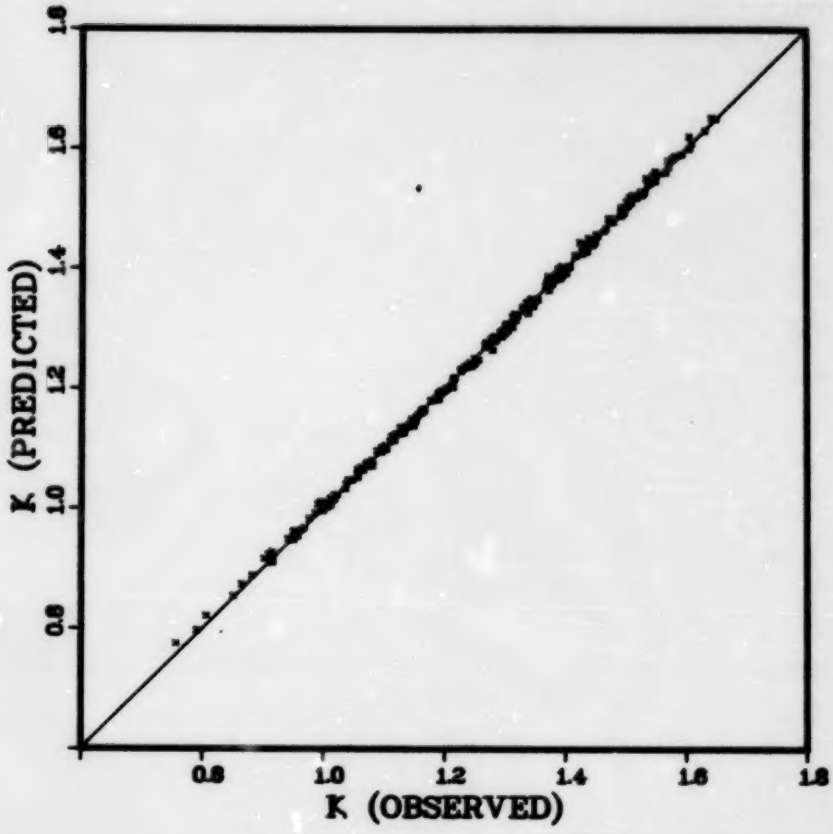

Fig. 9 - Correlation between experimental and calculated values (Equation 3) for the specific conductivities in the system $PbCl_2$-NaCl-KCl.

where X_i and M_i are the mole fraction and the molecular weight of component i in the solution and ρ is the density of the solution. Calculated molar volumes (cm^3) of 7 ternary and 4 binary compositions at different temperatures were found to fit an equation similar to Equation 3:

$$V_M = [c_0 + c_1y + c_2y^2 + c_3yt + c_4yt^2 + c_5ty^2] + T\,[d_0 + d_1y + d_2y^1 + d_3yt + d_4yt^2 + d_5ty^2] \qquad (6)$$

where

$c_0 = 38.922477$	$d_0 = 0.02234196$
$c_1 = 0.26814797 \times 10^2$	$d_1 = -0.04362468$
$c_2 = -0.73728819 \times 10^2$	$d_2 = 0.08424459$
$c_3 = 0.08204854 \times 10^2$	$d_3 = -0.01908987$
$c_4 = -0.60582923 \times 10^2$	$d_4 = 0.06740170$
$c_5 = 0.76969887 \times 10^2$	$d_5 = -0.09268133$

Standard error of estimate = $\pm 0.49\ cm^3$

By comparing V_M values based on density measurements (5-7) with those predicted by Equation 6, only one value differed by more than 2% (<3%) and hence the molar volume of ternary solutions may be calculated at any temperature, within the experimental region, with a reasonable accuracy.

The molar conductivities of all compositions investigated in this study were calculated at 500°C using Equations 2, 4 and 6 and are correlated to $PbCl_2$ mole fraction for 6 values of t in Figure 10. Equation 2 was chosen for the calculation of the specific conductivity since, unlike Equation 3, it does not assume any particular relationship between the conductivity and composition.

Equivalent conductivity is given by:

$$\Lambda_E = \kappa . V_E = \kappa \frac{\sum f_i E_i}{\rho} \qquad (7)$$

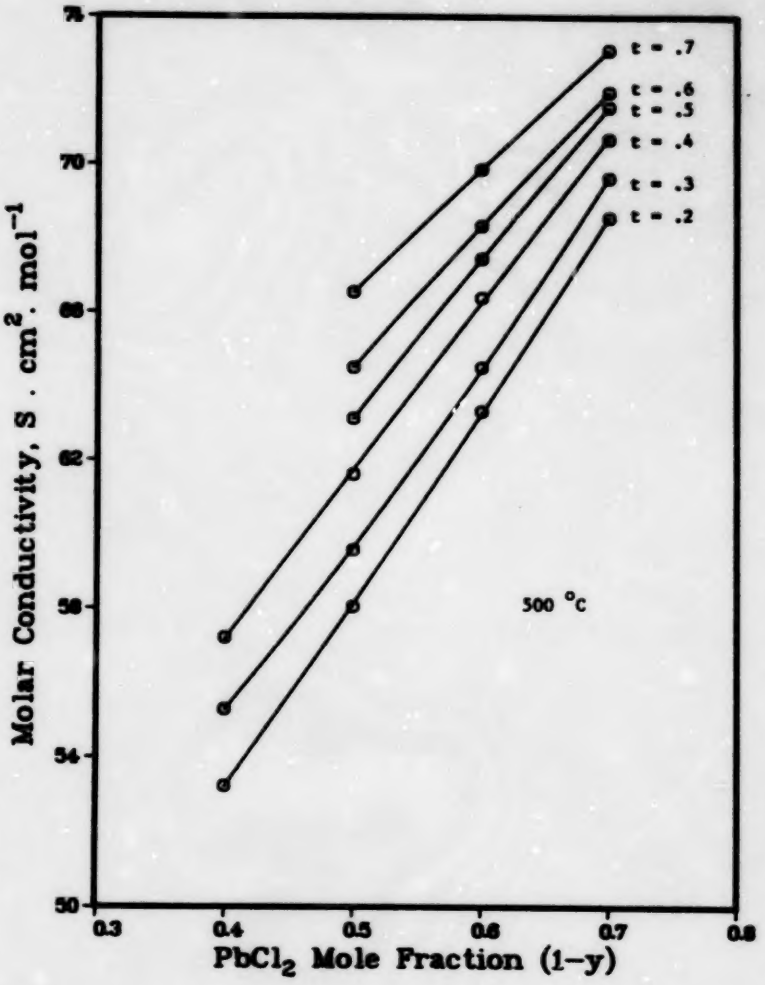

Fig. 10 - The dependence of the molar conductivities in the system $PbCl_2$-NaCl-KCl on $PbCl_2$ mole fraction at 500°C.

where V_E is the equivalent volume, f_i is the equivalent fraction and $E_i = M_i/z_i$ is the equivalent weight of component i; z_i is the number of moles of charge per mole of salt, i.e., 2 for $PbCl_2$ and 1 for KCl and NaCl. It can be shown that:

$$\sum f_i E_i = \frac{\sum X_i M_i}{\sum X_i z_i} \qquad (8)$$

and hence the equivalent conductivity can be calculated from

$$\Lambda_E = \kappa \frac{V_M}{\sum X_i z_i} = \frac{\Lambda_M}{\sum X_i z_i} \qquad (9)$$

Equivalent conductivities at 500°C are shown as functions of $PbCl_2$ mole fraction in Figure 11. Using equivalent conductivities, comparisons can be made on the basis of equal quantities of ionic charge, assuming the salts to be fully ionized. Differences in equivalent conductivity can therefore be interpreted in terms of ionic mobilities and ion-ion interactions, which in extreme cases may involve complex ion formation.

At the KCl/NaCl ratios corresponding to t=0.2 and 0.3 there is a marked decrease in equivalent conductivity with decreasing $PbCl_2$ mole fraction. Although 500°C is well below the liquidus temperatures in the KCl-NaCl system (12), data for this system at 750°C (9) give equivalent conductivities as 101.6 and 103.1 $S.cm^2\ equiv^{-1}$ for t=0.2 and t=0.3, respectively, both of which are well above the equivalent conductivity of $PbCl_2$ at 750°C, 76.5 $S.cm^2\ equiv^{-1}$. It would be reasonable to suppose, therefore, that equivalent conductivities for compositions with t=0.2 and t=0.3 might increase, as do the equivalent conductivities at t=0.5, 0.6 and 0.7, rather than decrease as the mole fraction of $PbCl_2$ decreases. Equivalent conductivities in the $PbCl_2$-KCl system (t=0) show minima at about 0.4 mole fraction $PbCl_2$ (7,8); this has been attributed to the formation of lead-chloride complex ions with low mobility (7,8,10). Support for this suggestion of complexes of the type $PbCl_n^{(2-n)}$ in the $PbCl_2$-KCl system comes from studies of Raman spectra (19), vapour pressures (20,21), and free energies derived from emf measurements (22).

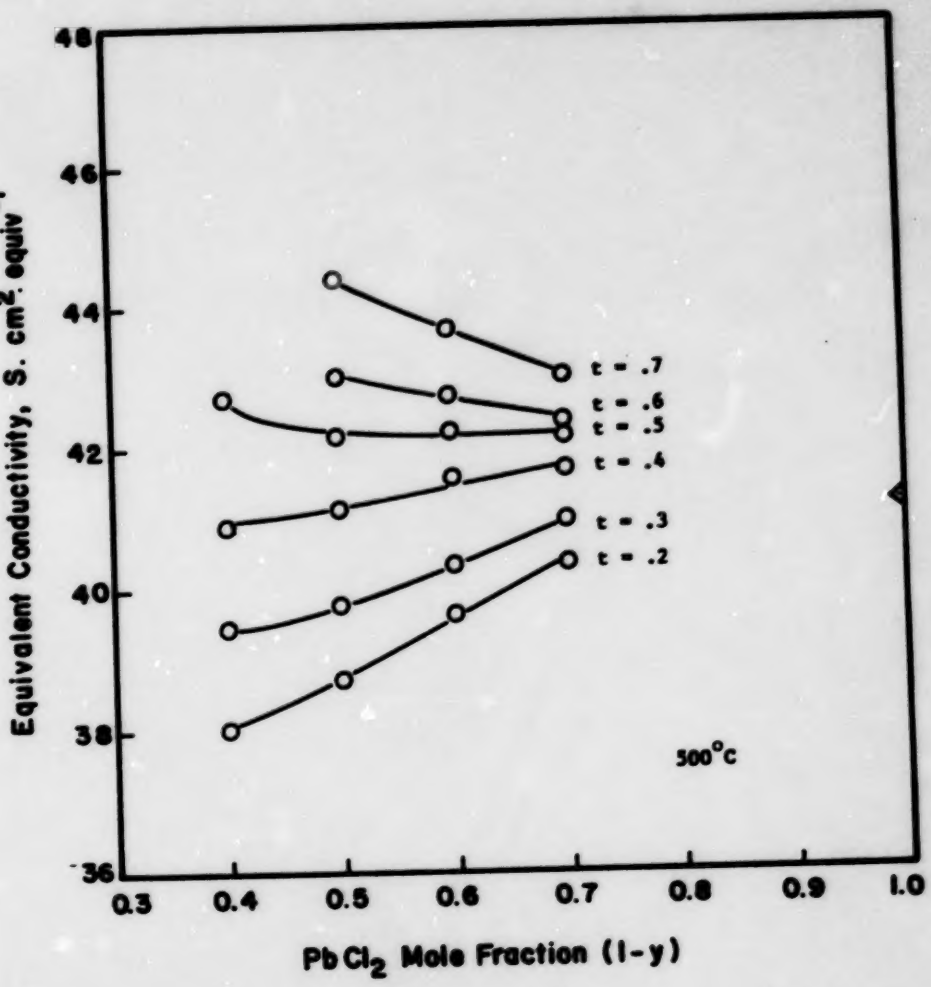

Fig. 11 - Equivalent conductivity in the system $PbCl_2$-NaCl-KCl at 500°C. $PbCl_2$ equivalent conductivity from Lantratov and Moiseeva (7).

The decrease in equivalent conductivity with decreasing $PbCl_2$ mole fraction for t=0.2 and t=0.3 at 500°C is probably indicative of an approach to a minimum that could not be attained because of the restricted range of single phase liquid compositions, as shown in Figure 6. It appears, therefore, that the effect of complex formation on conductivity can be observed in the $PbCl_2$-KCl-NaCl system near the $PbCl_2$-KCl boundary. This effect was less evident in the $PbCl_2$-KCl-LiCl system (4), where, at t=0.3, there was hardly any evidence of a minimum in equivalent conductivity.

The effects of complex formation between chloride and lead ions in alkali chloride - lead chloride systems have been found to increase with increasing radius of the alkali metal ion (10). The presence of smaller more polarizing cations appears to destabilize the complexes. Therefore the substitution of the smaller Na^+ ion (r=0.097 nm) for the K^+ ion (r=0.133 nm) would be expected to decrease the stability of the complexes and hence reduce the depressing effect that complex formation would have on conductivity. The destabilization of the complexes by substitution of Li^+ (r=0.068 nm) would be even greater than that produced by the substitution of Na^+ for K^+. Hence the effects of complex formation on electrical conductivity are less evident in the $PbCl_2$-LiCl-KCl system than in the $PbCl_2$-NaCl-KCl system.

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